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(54)【発明の名称】 排気ガス浄化用触媒とその担持方法

(57)【要約】

【目的】 触媒の熱的、機械的応力による劣化を緩和する。

【構成】 ペロブスカイト型複合酸化物、耐熱性酸化物及びジルコニアゾル、セリアゾル、イットリアゾルもしくはそれらの混合ゾル、又はZr、Ce、Yのうちの2以上を含む固溶体酸化物ゾルを純水に加え、ボールミルで12時間攪拌混合して得たスラリーをコーゼライト質の耐熱性ハニカム担体に塗布し、乾燥後、600℃で大気中3時間焼成してペロブスカイト型複合酸化物と耐熱性酸化物が均一にコーティングされた担体を得る。これに硝酸パラジウム水溶液を含浸させ、乾燥後、大気中で600℃で3時間焼成する。

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## 【特許請求の範囲】

【請求項1】 ペロブスカイト型複合酸化物と貴金属又はさらに助触媒である耐熱性酸化物が共存した触媒系が、ジルコニアゾル、セリアゾル、イットリアゾルもしくはそれらの混合ゾル、又はZr、Ce、Yのうちの2以上を含む固溶体酸化物ゾルを結合剤として含んで耐熱性担体に担持されていることを特徴とする排気ガス浄化用触媒。

【請求項2】 ペロブスカイト型複合酸化物粉末と金属酸化物ゾル又はさらに助触媒粉末を含む混合体に水を加え、攪拌混合してスラリーを形成し、そのスラリーを耐熱性担体にコーティングして焼成した後、そのコーティングされた担体に貴金属塩水溶液を含浸及び／又は吸着させ、焼成することを特徴とする排気ガス浄化用触媒の担持方法。

【請求項3】 金属酸化物ゾルの含有量はペロブスカイト型複合酸化物又はさらに耐熱性酸化物の含量100重量部に対して0.5～50重量部である請求項3に記載の担持方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は一酸化炭素(CO)、炭化水素(THC)及び酸化窒素(NO<sub>x</sub>)の浄化能力に優れた排気ガス浄化用三元触媒を耐熱性担体に担持させたものと、耐熱性担体にその触媒を担持する方法に関するものである。

## 【0002】

【従来の技術】排気ガス浄化用三元触媒としてはアルミナ単体にPt、Rh、Pdなどの貴金属を担持した貴金属触媒が実用化されて広く使用されている。また、希土類金属、アルカリ土類金属及び遷移金属から構成されるペロブスカイト型構造を有する複合酸化物は、CO、THC及びNO<sub>x</sub>を浄化する安価な排気ガス浄化用三元触媒として実用化が期待されている(特開昭59-87046号公報、特開昭60-82138号公報参照)。このペロブスカイト型複合酸化物はCO、HCの浄化能力は優れているが、NO<sub>x</sub>の浄化能力がやや劣っており、自動車排気ガス用の三元触媒として実用に供するには十分でない。そこで、ペロブスカイト型複合酸化物触媒のNO<sub>x</sub>浄化能力を高めるために貴金属を共存させている(特開平1-168343号公報、特開平2-90947号公報参照)。触媒活性を一層高め、耐熱性も高めるために、ペロブスカイト型複合酸化物触媒とともにCeO<sub>2</sub>、(CeZrY)O<sub>2</sub>、SrZrO<sub>3</sub>などの耐熱性酸化物を助触媒として共存させることも行なわれている。

【0003】これらの触媒はコーセライトハニカム担体などの耐熱性担体に担持されて使用される。その担持方法は、ペロブスカイト型複合酸化物粉末又はさらにそれに耐熱性酸化物粉末などの助触媒を加えた粉体に水を加え、ボールミル等で粉碎あるいは攪拌し混合してスラ

リーを形成した後、そのスラリーを担体に塗布し、焼成した後、貴金属水溶液をそのコーティング担体中含浸又は吸着させた後に焼成する方法である。

## 【0004】

【発明が解決しようとする課題】自動車排気ガス浄化用触媒は速い流速のガスを受け、高温に曝され、加熱と冷却を繰り返し受け、さらに振動や衝撃などの機械的応力を受ける環境下で長期間にわたって使用される。その結果、担体から触媒有効成分が剥離し脱落してしまう問題が生じる。従来の貴金属系触媒(Pt-Pd-Rh)では、触媒を担持するアルミナ粒子とハニカム担体との間の結合剤としてアルミナゾルが用いられている。しかし、希土類金属を含むペロブスカイト酸化物触媒にアルミナゾルを用いると、アルミナゾルはペロブスカイト(ABO<sub>3</sub>)中のAサイトの希土類金属と反応しやすく、使用中にLnAlO<sub>3</sub>化合物(LnはCeを除く希土類金属)を生成して触媒活性を低下させる問題が生じる。本発明は触媒有効成分が反応や剥離等により活性が低下するのを防いだ担持状態の排気ガス浄化用触媒と、触媒成分を担体に担持させる方法とを提供することを目的とするものである。

## 【0005】

【課題を解決するための手段】本発明ではペロブスカイト型複合酸化物と貴金属又はさらに助触媒である耐熱性酸化物が共存した触媒系が、ジルコニアゾル、セリアゾル、イットリアゾルもしくはそれらの混合ゾル、又はZr、Ce、Yのうちの2以上を含む固溶体酸化物ゾルを結合剤として含んで耐熱性担体に担持されている。結合剤のゾルの例は次のようなものである。ジルコニアゾルとしては例えば日産化学工業株式会社の製品「NZS-20A」、「NZS-30A」、「NZS-30B」、ジルコニア・イットリアゾルとしては例えば日産化学工業株式会社の製品「NZS-20A3Y」、セリアゾルの例としては多木化学株式会社の製品「ニードラールW-15-01」、イットリアゾル例としては多木化学株式会社の製品「酸化イットリウムゾル」を用いることができる。これらの金属酸化物ゾルの固形分の含有量をペロブスカイト型複合酸化物又は更に耐熱性酸化物との含量の100重量部に対して0.5～50重量部、より好ましくは1～10重量部とする。金属酸化物ゾルの含有量が0.5重量部未満の場合は結合剤としての効果がみられず、50重量部より多くなるとマスキングにより触媒活性が低下するからである。

【0006】ペロブスカイト型複合酸化物は一般式Ln<sub>1-x</sub>A<sub>x</sub>MO<sub>3</sub>(LnはCeを除く希土類金属、AはCe又はアルカリ土類金属、MはMn、Fe、Co、Ni、Cu、Pd及びRuからなる遷移金属で、いずれも1種又は2種以上、0<x<1)で示される酸化物である。貴金属はPd、Pt、Ru、Rh及びIrからなる群より選ばれた1種又は2種以上の金属であり、特にP

dは低湿浄化活性とNO<sub>x</sub>浄化活性を向上させるものであり、好ましい。

【0007】助触媒は高温における浄化活性を高めるためのものであり、Ce及びZr、又はさらにCe以外の希土類金属を含み少なくとも一部が複合酸化物及び／もしくは固溶体となっている耐熱性酸化物、又はCeからなる耐熱性酸化物である。助触媒の例としてはCeO<sub>2</sub>、(CeZr)O<sub>2</sub>、他、(CeZrY)O<sub>2</sub>、(CeZrLa)O<sub>2</sub>、(CeZrNd)O<sub>2</sub>など、一般式(CeZrLn)O<sub>2</sub>(LnはCeを除く希土類金属)で表わされる複合酸化物が好ましい。また、CeO<sub>2</sub>よりは(CeZr)O<sub>2</sub>の方が高温における浄化活性を高める効果に優れ、更に(CeZrLn)O<sub>2</sub>の方が高温における浄化活性を高める効果に優れているので、より好ましい。

【0008】本発明の担持方法は、ペロブスカイト型複合酸化物粉末と金属酸化物ゾル又はさらに助触媒粉末を含む混合体に水を加え、攪拌混合してスラリーを形成し、そのスラリーを耐熱性担体にコーティングして焼成した後、そのコーティングされた担体に貴金属水溶液を含浸及び／又は吸着させ、焼成する。コーティングされた担体に貴金属水溶液を含浸及び／又は吸着させる際、ペロブスカイト型複合酸化物と金属酸化物ゾルとの混合物100重量部、又はペロブスカイト型複合酸化物、耐熱性酸化物及び金属酸化物ゾルとの混合物100重量部に対して総貴金属換算で0.2～5.0重量部を含む貴金属塩水溶液を用いて貴金属を含浸及び／又は吸着担持させ、乾燥後250～800℃の温度で焼成する。このときの貴金属水溶液のpHを10より大きいアルカリ性とするか、4より小さい酸性とすることにより、低温でも触媒活性の高いものが得られることが本発明者によって見出されており、別途特許出願中である。

【0009】貴金属水溶液をアルカリ性とする場合、テトラアミンパラジウムジクロライドPd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>、やテトラアミンパラジウム水酸塩Pd(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>などの塩基性水溶液にアンモニア水や酸を添加してpH>10になるように調製して用いるか、PdCl<sub>2</sub>、PtCl<sub>2</sub>、RuCl<sub>3</sub>・3H<sub>2</sub>Oなどの塩化物、Pd(NO<sub>3</sub>)<sub>2</sub>、Ru(NO<sub>3</sub>)<sub>3</sub>、Rh(NO<sub>3</sub>)<sub>3</sub>などの硝酸塩、又はPd(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>、Pt(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>などのジニトロジアミン塩などの酸性水溶液にアンモニア水を添加してpH>10になるように調製して用いる。

【0010】貴金属水溶液を酸性とする場合、pH4以下に調整した貴金属塩水溶液にペロブスカイト型複合酸化物を浸漬すると、結晶中の元素が一部溶出し、溶出せず残存したペロブスカイト型複合酸化物粉末や耐熱性酸化物粉末を核としてその周りに貴金属を含む複数の塩が付着した状態となる。それを、乾燥した後、大気中で焼成することにより、核の周囲に貴金属を固溶したペロブスカイト型複合酸化物結晶が形成されて酸化物の二重構

造になる。再結晶化したペロブスカイト型複合酸化物結晶に固溶しきれなかった余分の貴金属は金属状態又は貴金属酸化物として分散する。貴金属水溶液を酸性とする場合の水溶性貴金属塩としては、PdCl<sub>2</sub>、PtCl<sub>2</sub>、RuCl<sub>3</sub>・3H<sub>2</sub>Oなどの塩化物、Pd(NO<sub>3</sub>)<sub>2</sub>、Ru(NO<sub>3</sub>)<sub>3</sub>、Rh(NO<sub>3</sub>)<sub>3</sub>などの硝酸塩、Pd(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>、Pt(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>などのジニトロジアミン塩など、水溶液が強酸性を示すものが好ましい。

#### 10 【0011】

【発明の効果】本発明ではペロブスカイト型複合酸化物粉末又はさらに助触媒である耐熱性酸化物を含んだものを耐熱性担体に担持させる際、結合剤としてジルコニアゾル、セリアゾル、イットリアゾルもしくはそれらの混合ゾル、又はZr、Ce、Yのうち2種類以上を含む固溶体酸化物ゾルを使用し、焼成することにより、ゾルに含まれた揮発分が飛散して微細で比表面積の大きい酸化物となり更に触媒系と担体との機械的結合力を高め、触媒が使用される環境下での熱的、機械的な応力による触媒の劣化を緩和し、長期間の使用に耐え得るようになる。またこれらの金属酸化物ゾルは触媒をマスキングしたり、使用中に触媒と反応して触媒活性を低下させることがない。

#### 【0012】

##### 【実施例】

(実施例1) 担体に用いるペロブスカイト型複合酸化物と耐熱性酸化物は次のように作成した。ペロブスカイト型複合酸化物を共沈法により作成するために、硝酸ランタン103.9g、硝酸セリウム26.1g、硝酸コバルト34.9g、硝酸鉄72.7gを純水に溶解した水溶液0.3リットルと、中和共沈剤としての炭酸ナトリウム50gを溶解した水溶液0.5リットルとを用意し、中和共沈剤を先の水溶液に滴下し、共沈物を得た。その共沈物を十分水洗し、濾過した後、真空乾燥した。これを600℃で3時間大気中で焼成後、粉碎し、その後、800℃で3時間大気中で焼成を行ない、さらに粉碎してペロブスカイト型複合酸化物(La<sub>0.8</sub>Ce<sub>0.2</sub>)(Co<sub>0.8</sub>Fe<sub>0.2</sub>)O<sub>3</sub>の粉末を作成した。

【0013】耐熱性酸化物を作成するために、市販の高比表面積の酸化セリウム粉末(CeO<sub>2</sub>比表面積170m<sup>2</sup>/g、純度99.9%/TREO(全希土類酸化物))111.9gを用意し、これにオキシ硝酸ジルコニウム(ZrO(NO<sub>3</sub>)<sub>2</sub>)水溶液(液比重1.51、液中にZrO<sub>2</sub>換算で25.0重量%含まれる)147.9g、及び硝酸イットリウム(Y(NO<sub>3</sub>)<sub>3</sub>)水溶液(液比重1.62、液中にY<sub>2</sub>O<sub>3</sub>換算で21.7重量%含まれる)26.0gを加え、よく攪拌して混合しながら110℃で10時間大気中で乾燥した。その後、大気中で600℃で3時間焼成を行ない、(Ce<sub>0.8</sub>Zr<sub>0.2</sub>Y<sub>0.2</sub>)O<sub>3</sub>複合酸化物を約150g得た。

【0014】スラリーコート担体を得るために、先のペロブスカイト型複合酸化物( $\text{La}_{0.9}\text{Ce}_{0.1}\text{O}_3$ 、 $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_3$ 、 $\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3$ )の50重量部と、耐熱性酸化物( $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_3$ )の50重量部と、ジルコニアゾルである日産化学工業株式会社製NZS-30B(固形分30.44重量%、 $\text{pH}=10.62$ )を固形分換算で5重量部となるように純水100重量部に加え、ボールミルで12時間混合して得たスラリーをコージェライト質の耐熱性ハニカム担体に流し込み、余部のスラリーを空気流で吹き払い、乾燥(例えば130°Cで24時間)させた後、600°Cで大気中3時間焼成してペロブスカイト型複合酸化物と耐熱性酸化物が均一にコーティングされた担体を得た。

【0015】貴金属としてPdを担持させるために、ペロブスカイト型複合酸化物及び耐熱性酸化物の合計100重量部に対してPd換算で2.5重量部となるように秤量した硝酸パラジウム水溶液(田中貴金属工業株式会社の製品で、Pd金属分4.4重量%)56.8重量部を希硝酸100重量部に溶かした。この溶液の $\text{pH}$ は0.2であった。この溶液の全量を上記のコーティングハニカム担体に含浸させた後、130°Cで24時間乾燥し、大気中で600°Cで3時間焼成した。

【0016】(実施例2)実施例1と同様にして、ただし結合剤の金属酸化物ゾルとしてジルコニアゾルに代えてセリアゾルである多木化学株式会社製ニードラールW-10-01(固形分10.1重量%、 $\text{pH}=5.0$ )を用い、その含有量を固形分換算で2重量部とした。

【0017】(実施例3)実施例1と同様にして、ただし結合剤の金属酸化物ゾルとしてジルコニアゾルである日産化学工業株式会社製NZS-30B(固形分30.44重量%、 $\text{pH}=10.62$ )を固形分換算で1重量部と、セリアゾルである多木化学株式会社製ニードラール

W10-01(固形分10.1重量%、 $\text{pH}=5.0$ )を固形分換算で5重量部となるようにともに使用した。

【0018】(実施例4)実施例1と同様にして、ただし耐熱性酸化物として市販の高比表面積酸化セリウム( $\text{CeO}_2$ 、比表面積170 $\text{m}^2/\text{g}$ 、純度99.9%/TREO)を用いて50重量部とし、また結合剤の金属酸化物ゾルとしてジルコニアに代えてジルコニア・イットリアゾルである日産化学工業株式会社製NZS-20A3Y(固形分10.77重量%、 $\text{pH}=4.12$ )を用い、その含有量を固形分換算で10重量部とした。

【0019】(比較例a)実施例1と同様にして、ただし結合剤の金属酸化物ゾルを使用しなかった。

(比較例b)実施例4と同様にして、ただし結合剤の金属酸化物ゾルを使用しなかった。

(比較例c)実施例1と同様にして、ただし結合剤の金属酸化物ゾルとしてアルミナゾルである日産化学工業株式会社製AS-100(固形分10.23重量%、 $\text{pH}=3.91$ )を使用し、その含有量を10重量部とした。

【0020】実施例と比較例の触媒を、大気雰囲気中で800°Cに保持された電気炉へ投入して15分間保持し、電気炉から出して500,000Paに加圧されたエアブローで20分間冷却するテストを500サイクル繰り返した後、 $A/F=14.6$ でエンジンを作動させたときの排気ガスを用い、熱交換器にてその排気ガス温度を上昇させていき、排気ガス中の $\text{NO}_x$ 、CO、THCが初期濃度の50%に低下した温度(50%浄化温度)を求めたテスト結果を表1に示す。このときの触媒を通過する排気ガスの空間速度(SV)は約100,000

【0021】

【表1】

	ゾル (重量部)	50%浄化温度 (℃)		
		NO <sub>x</sub>	CO	THC
実施例1	ジルコニアゾル 5	324	321	350
実施例2	セリアゾル 2	348	364	364
実施例3	ジルコニア1 セリア5	319	320	327
実施例4	ジルコニア・イットリア 10	349	353	366
比較例a	なし	378	421	>500
比較例b	なし	>500	411	>500
比較例c	アルミナゾル 10	>500	>500	>500

【0022】表1中でゾルの含有量はペロブスカイト型複合酸化物と耐熱性酸化物の含量を100重量部としたときの固形分換算重量部を表わしている。この結果から、結合剤として従来のアルミナゾルを使用した場合には使用中に触媒活性が低下していることがわかる。結合

20 剤としてゾルを用いない場合は、触媒の劣化が進み50%浄化温度が高くなってきている。それに対し、本発明では選ばれたゾルの効果により熱的、機械的な応力による触媒の劣化が緩和され、長時間の使用に耐え得るようになっている。

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(71)Applicant : DAIHATSU MOTOR CO LTD

(22)Date of filing : 09.03.1992

(72)Inventor : TANAKA HIROHISA  
SODA AKIRA

## (54) CATALYST FOR CLEANING EXHAUST GAS AND DEPOSITING METHOD THEREFOR

## (57)Abstract:

PURPOSE: To retard deterioration of a catalyst by thermal and mechanical stress.

CONSTITUTION: A perovskite type multiple oxide, a heat resistant oxide and a zirconia sol, ceria sol, yttria sol or these mixed sol or a solid solution sol containing two or more of Zr, Ce, Y are added into a pure water and are stirred and mixed in a ball mill for 12 hours and the obtained slurry is applied to a cordierite heat resistant honeycomb carrier and is dried and calcined at 600° C in an atmosphere for 3 hours to obtain the carrier uniformly coated with the perovskite multiple oxide and the heat resistant oxide. The carrier is impregnated with a palladium nitrate aq. solution, is dried and is calcined at 600° C for 3 hours in an atmosphere.

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<u>CLAIMS</u>	<u>DETAILED DESCRIPTION</u>	<u>TECHNICAL FIELD</u>	<u>PRIOR ART</u>	<u>EFFECT OF THE INVENTION</u>	<u>TECHNICAL PROBLEM</u>	<u>MEANS</u>	<u>EXAMPLE</u>
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**CLAIMS**

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[Claim(s)]

[Claim 1] The catalyst for exhaust gas clarification characterized by the catalyst system with which a perovskite mold multiple oxide, noble metals, or the heat-resistant oxide that is a co-catalyst further coexisted being supported by heat-resistant support including a zirconia sol, a ceria sol, yttria sols, those mixed sols, or the solid-solution oxide sol containing two or more [ of Zr, Ce, and the Y ] as a binder.

[Claim 2] The support approach of the catalyst for exhaust gas clarification which adds water to perovskite mold multiple oxide powder, a metallic-oxide sol, or the mixture that contains co-catalyst powder further, carries out churning mixing, and is characterized for a noble-metals salt water solution by impregnation and/or making it adsorb and calcinating at the support by which coating was carried out after forming a slurry, coating heat-resistant support with the slurry and calcinating it.

[Claim 3] The content of a metallic-oxide sol is a PUROBUSU kite mold multiple oxide or the support approach according to claim 3 which is 0.5 – 50 weight section to the total amount 100 weight section of a heat-resistant oxide further.

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[Translation done.]



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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the thing which made heat-resistant support support the three way component catalyst for exhaust gas clarification excellent in the clarification capacity of a carbon monoxide (CO), a hydrocarbon (THC), and nitrogen oxide (NOx), and the approach of supporting the catalyst to heat-resistant support.

[0002]

[Description of the Prior Art] As a three way component catalyst for exhaust gas clarification, the precious metal catalyst which supported noble metals, such as Pt, Rh, and Pd, is put in practical use by the alumina simple substance, and it is widely used for it. Moreover, utilization is expected as a cheap three way component catalyst for exhaust gas clarification with which the multiple oxide which has the perovskite type structure which consists of a rare earth metal, an alkaline earth metal, and transition metals purifies CO, THC, and NOx (refer to JP,59-87046,A and JP,60-82138,A). Although CO and the clarification capacity of HC are excellent, this perovskite mold multiple oxide is a little inferior in the clarification capacity of NOx, and they are not enough to present practical use as a three way component catalyst for motor exhaust. Then, noble metals are made to live together in order to heighten the NOx clarification capacity of a perovskite mold multiple oxide catalyst (refer to JP,1-168343,A and JP,2-90947,A). In order to raise catalytic activity further and to also raise thermal resistance, also making heat-resistant oxides, such as CeO<sub>2</sub>, O (CeZrY)<sub>2</sub>, and SrZrO<sub>3</sub>, live together as a co-catalyst with a perovskite mold multiple oxide catalyst is performed.

[0003] These catalysts are supported and used for heat-resistant support, such as cordierite honeycomb support. After the support approach applies to support the slurry after adding water to perovskite mold multiple oxide powder or the fine particles which added co-catalysts, such as heat-resistant oxide powder, to it further, grinding, or agitating and mixing with a ball mill etc. and forming a slurry and calcinates it, it is an approach of calcinating a noble-metals water solution to the coating support impregnation or after making it adsorbing.

[0004]

[Problem(s) to be Solved by the Invention] The catalyst for automobile exhaust air gas cleanups is used over a long period of time under the environment where receive the gas of the quick rate of flow, and it is put to an elevated temperature, repeat and receive heating and cooling, and mechanical stress, such as an oscillation and an impact, is received further. Consequently, the problem on which a catalyst active principle exfoliates and drops out of support arises. With the conventional noble-metals system catalyst (Pt-Pd-Rh), alumina sol is used as a binder between the alumina particles and honeycomb support which support a catalyst. However, if alumina sol is used for the perovskite oxide catalyst containing a rare earth metal, alumina sol will tend to react with the rare earth metal of A site in perovskite (ABO<sub>3</sub>), and the problem which LnAlO<sub>3</sub> compound (rare earth metal excluding [ Ln ] Ce) is generated [ problem ], and reduces catalytic activity while in use will produce it. This invention aims at offering the catalyst for exhaust gas clarification of the support condition from which the catalyst active principle protected that activity fell by the reaction, exfoliation, etc., and the method of making support support a catalyst component.

[0005]

[Means for Solving the Problem] The catalyst system with which a perovskite mold multiple oxide, noble metals, or the heat-resistant oxide that is a co-catalyst further coexisted is supported with this invention by heat-resistant support including a zirconia sol, a ceria sol, yttria sols, those mixed sols, or the solid-solution oxide sol containing two or more [ of Zr, Ce, and the Y ] as a binder. The example of the sol of a binder is as follows. As a zirconia sol, for example, the product "NZS-20A" of Nissan Chemical Industries, Ltd., "NZS-30A", "NZS-30B", As a zirconia yttria sol, for example, the product of Nissan Chemical Industries, Ltd. "NZS-20 A3Y", As an example of a ceria sol, the product "a yttrium oxide sol" of Taki Chemical Co., Ltd. can be used as the product "need RARU W-15-01" of Taki Chemical Co., Ltd., and an example of a yttria sol, the content of the solid content of these metallic-oxide sols — a PUROBUSU kite mold multiple oxide — or — further — the 100 weight sections of a total amount with a heat-resistant oxide — receiving — 0.5 - 50 weight section — it considers as 1 - 10 weight section more preferably. It is because catalytic activity will fall with masking if the effectiveness as a binder is not seen but it increases more than 50 weight sections, when the content of a metallic-oxide sol is under the 0.5 weight section.

[0006] A perovskite mold multiple oxide is an oxide shown by general formula Ln<sub>1-x</sub>A<sub>x</sub>MO<sub>3</sub> (the rare earth metal except Ce and A are the transition metals which consist of Mn, Fe, Co, nickel, Cu, Pd, and Ru, and Ln is [ Ce or alkaline earth metal, and M ] all one sort or two sorts or more, and 0 < x < 1). Noble metals are one sort or two sorts or more of metals chosen from the group which consists of Pd, Pt, Ru, Rh, and Ir, and especially Pd raises damp clarification activity and NOx clarification activity, and is desirable.

[0007] A co-catalyst is for raising hot clarification activity, and is Ce and Zr, the heat-resistant oxide with which at least the part serves as a multiple oxide and/, or the solid solution including rare earth metals other than Ce further, or a heat-resistant oxide which consists of Ce. As for the multiple oxide expressed with a general formula (CeZrLn) O<sub>2</sub> (rare earth metal excluding [ Ln ] Ce), as an example of a co-catalyst, O (CeZrY)<sub>2</sub>, O (CeZrLa)<sub>2</sub>, O (CeZrNd)<sub>2</sub>, etc. besides CeO<sub>2</sub> and O (CeZr)<sub>2</sub> are desirable. Moreover, since two

are excelled in the effectiveness that the direction of  $\text{CeOO}(\text{CeZr})_2$  raises hot clarification activity and it excels in the effectiveness that the direction of  $\text{O}_2$  raises hot clarification activity further ( $\text{CeZrLn}$ ), it is more desirable.

[0008] The support approach of this invention adds water to perovskite mold multiple oxide powder, a metallic-oxide sol, or the mixture that contains co-catalyst powder further, carries out churning mixing, forms a slurry, after it coats heat-resistant support with the slurry and calcinates it, makes a noble-metals water solution sink in and/or stick to the support by which coating was carried out, and calcinates it. Using the noble-metals salt water solution which contains the 0.2 – 5.0 weight section for a noble-metals water solution by total noble-metals conversion to the mixture 100 weight section with the mixture 100 weight section of a perovskite mold multiple oxide and a metallic-oxide sol or a perovskite mold multiple oxide, a heat-resistant oxide, and a metallic-oxide sol impregnation and/or in case it is made to adsorb, the support by which coating was carried out is made to sink in and/or adsorption support, and noble metals are calcinated at the temperature of 250–800 degrees C after desiccation to it. By making pH of the noble-metals water solution at this time into larger alkalinity than 10, or considering as acidity smaller than 4, it is found out by this invention person that the high thing of catalytic activity is obtained also at low temperature, and it is patent pending separately.

[0009] the case where a noble-metals water solution is made into alkalinity — tetra— amine palladium dichloride  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$  — tetra— whether it prepares and uses so that aqueous ammonia and an acid may be added in basic water solutions, such as amine palladium oxalate  $\text{Pd}(\text{NH}_3)_4(\text{OH})_2$ , and it may be set to  $\text{pH} > 10$  Nitrates, such as chlorides, such as  $\text{PdCl}_2$ ,  $\text{PtCl}_2$ , and  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , and  $\text{Pd}(\text{NO}_3)_2$ ,  $\text{Ru}(\text{NO}_3)_3$ ,  $\text{Rh}(\text{NO}_3)_3$ . Or it prepares and uses so that aqueous ammonia may be added to aqueous acids, such as dinitro diamine salts, such as  $\text{Pd}(\text{NO}_2)_2(\text{NH}_3)_2$  and  $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ , and it may be set to  $\text{pH} > 10$ .

[0010] If a perovskite mold multiple oxide is immersed in the noble-metals salt water solution adjusted to four or less pH when making a noble-metals water solution into acidity, it will be in the condition that two or more salts which contain noble metals in the surroundings of it by using as a nucleus the perovskite mold multiple oxide powder and the heat-resistant oxide powder with which a part of element under crystal was eluted, and eluted and remained adhered. By calcinating it in atmospheric air, after drying, the perovskite mold multiple oxide crystal which dissolved noble metals is formed in a nuclear perimeter, and it becomes the dual structure of an oxide. The noble metals of the excess which was not able to dissolve into the perovskite mold multiple oxide crystal which recrystallized are distributed as a metal condition or a noble-metals oxide. As a water-soluble noble-metals salt in the case of making a noble-metals water solution into acidity, dinitro diamine salts of that a water solution indicates strong acid nature to be, such as nitrates, such as chlorides, such as  $\text{PdCl}_2$ ,  $\text{PtCl}_2$ , and  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , and  $\text{Pd}(\text{NO}_3)_2$ ,  $\text{Ru}(\text{NO}_3)_3$ ,  $\text{Rh}(\text{NO}_3)_3$ ,  $\text{Pd}(\text{NO}_2)_2(\text{NH}_3)_2$ , and  $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ , etc. are desirable.

[0011]

[Effect of the Invention] When making heat-resistant support support with this invention the thing containing PUROBUSU kite mold multiple oxide powder or the heat-resistant oxide which is a co-catalyst further, By using and calcinating a zirconia sol, a ceria sol, yttria sols, those mixed sols, or a solid-solution oxide sol including two or more kinds in Zr, Ce, and Y as a binder The volatile matter contained in the sol disperses, and it can be detailed, and can become an oxide with a large specific surface area, the mechanical bonding strength of a catalyst system and support can be heightened further, degradation of the catalyst by the thermal and mechanical stress under the environment where a catalyst is used can be eased, and it can be equal now to a prolonged activity. Moreover, these metallic-oxide sols do not mask a catalyst, or do not reduce [ be / it / under / activity / reaction ] catalytic activity with a catalyst.

[0012]

[Example]

(Example 1) The perovskite mold multiple oxide and the heat-resistant oxide which are used for support were created as follows. In order to create a perovskite mold multiple oxide with a coprecipitation method, 103.9g of lanthanum nitrates, 26.1g of cerium nitrates, 34.9g of cobalt nitrates, 0.3l. of water solutions which dissolved 72.7g of iron nitrate in pure water, and 0.5l. of water solutions which dissolved 50g of sodium carbonates as a neutralization coprecipitater were prepared, the neutralization coprecipitater was dropped at the previous water solution, and the coprecipitate was obtained. The vacuum drying was carried out, after rinsing the coprecipitate enough and filtering it. This was ground after baking in 3-hour atmospheric air at 600 degrees C, and it calcinated in 3-hour atmospheric air at 800 degrees C after that, it ground further, and the powder of the perovskite mold multiple oxide ( $\text{La}_{0.8}\text{Ce}_{0.2}(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3$ ) was created.

[0013] In order to create a heat-resistant oxide Cerium oxide powder of a commercial high specific surface area (2/g  $\text{CeO}_2$  specific surface area of 170m) 99.9% of purity and TREO(all rare earth oxides)111.9g are prepared. To this, 147.9g (contained 25.0% of the weight by  $\text{ZrO}_2$  conversion in liquid density 1.51 and liquid) of oxy-zirconium-nitrate ( $\text{ZrO}_2(\text{NO}_3)$ ) water solutions, And 26.0g (contained 21.7% of the weight by  $2\text{OY}_3$  conversion in liquid density 1.62 and liquid) of nitric-acid yttrium ( $\text{Y}(\text{NO}_3)_3$ ) water solutions was added, and it dried in 10-hour atmospheric air at 110 degrees C, having agitated well and mixing. Then, baking was performed at 600 degrees C in atmospheric air for 3 hours, and about 150g of  $\text{O}(\text{Ce}_{0.65}\text{Zr}_{0.30}\text{Y}_{0.05})_2$  multiple oxides was obtained.

[0014] In order to obtain slurry coat support, they are 50 weight sections of the previous perovskite mold multiple oxide ( $\text{La}_{0.8}\text{Ce}_{0.2}(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3$ ), 50 weight sections of the heat-resistant oxide ( $\text{Ce}_{0.65}\text{Zr}_{0.30}\text{Y}_{0.05})\text{O}_2$ , NZS[ by Nissan Chemical Industries, Ltd. ]-30B which is a zirconia sol (30.44 % of the weight of solid content)  $\text{pH}=10.62$  is added to the pure-water 100 weight section so that it may become 5 weight-sections by solid content conversion. The slurry which mixed for 12 hours and was obtained with the ball mill is slushed into the heat-resistant honeycomb support of the quality of cordierite. After blowing off and drying the slurry of the complementary section by airstream (it is 24 hours at 130 degrees C), the support which is calcinated among atmospheric air at 600 degrees C for 3 hours and by which coating of a perovskite mold multiple oxide and the heat-resistant oxide was carried out to homogeneity was obtained.

[0015] In order to make Pd support as noble metals, the palladium nitrate water-solution (with product of Tanaka Kikinzoku Kogyo, Inc., it is 4.4 % of the weight by Pd metal) 56.8 weight section which carried out weighing capacity so that it might become the 2.5 weight sections by Pd conversion to a total of 100 weight sections of a perovskite mold multiple oxide and a heat-resistant oxide was melted in the aqua-fortis 100 weight section. pH of this solution was 0.2. After carrying out impregnation of the whole quantity of this solution

to the above-mentioned coating honeycomb support, it dried at 130 degrees C for 24 hours, and calcinated at 600 degrees C in atmospheric air for 3 hours.

[0016] (Example 2) Like the example 1, it replaced with the zirconia sol as a metallic-oxide sol of a binder, however the content was made into 2 weight sections by solid content conversion using need RARU W-10-01 (10.1 % of the weight of solid content, pH=5.0) by Taki Chemical Co., Ltd. which is a ceria sol.

[0017] (Example 3) the Taki Chemical Co., Ltd. make which is 1 weight section and a ceria sol in solid content conversion like an example 1 about NZS[ by Nissan Chemical Industries, Ltd. ]-30B (30.44 % of the weight of solid content, pH=10.62) which is a zirconia sol as a metallic-oxide sol of a binder — need RARU W10-01 (10.1 % of the weight of solid content, pH=5.0) was used so that it might become [ both ] 5 weight sections by solid content conversion.

[0018] (Example 4) Make it be the same as that of an example 1. However, it considered as 50 weight sections using commercial high specific-surface-area cerium oxide (CeO<sub>2</sub>, specific-surface-area 170m<sup>2</sup>/g, 99.9% of purity, TREO) as a heat-resistant oxide, and it replaced with the zirconia as a metallic-oxide sol of a binder, and the content was made into 10 weight sections by solid content conversion using NZS[ by Nissan Chemical Industries, Ltd. ]-20 A3Y (10.77 % of the weight of solid content, pH=4.12) which is a zirconia yttria sol.

[0019] ((a) The example of a comparison) The metallic-oxide sol of a binder was not used like the example 1.

((b) The example of a comparison) The metallic-oxide sol of a binder was not used like the example 4.

((c) The example of a comparison) the Nissan Chemical Industries, Ltd. make which is alumina sol as a metallic-oxide sol of a binder like an example 1 — AS-100 (10.23 % of the weight of solid content, pH=3.91) was used, and the content was made into 10 weight sections.

[0020] The catalyst of an example and the example of a comparison is supplied to the electric furnace held in the atmospheric-air ambient atmosphere at 800 degrees C. The test cooled for 20 minutes by the Ayr blow which held for 15 minutes, took out from the electric furnace, and was pressurized by 500,000Pa After 500 cycle \*\*\*\*\*, Using the exhaust gas when operating an engine by A/F=14.6, the exhaust gas temperature is raised in a heat exchanger, and the test result which searched for the temperature (50% clarification temperature) to which NO<sub>x</sub>, CO, and THC in exhaust gas fell to 50% of initial concentration is shown in a table 1. The space velocity (SV) of the exhaust gas which passes the catalyst at this time was adjusted so that it might be set to about 100,000/hr.

[0021]

[A table 1]

	ゾ ル (重量部)	50%浄化温度 (℃)		
		NO <sub>x</sub>	CO	THC
実施例 1	ジルコニアゾル 5	324	321	350
実施例 2	セリアゾル 2	348	364	364
実施例 3	ジルコニア 1 セリア 5	319	320	327
実施例 4	ジルコニア・イットリア 10	349	353	366
比較例 a	なし	378	421	>500
比較例 b	なし	>500	411	>500
比較例 c	アルミナゾル 10	>500	>500	>500

[0022] The content of a sol expresses the solid content equivalent weight section when making the total amount of a perovskite mold multiple oxide and a heat-resistant oxide into the 100 weight sections in a table 1. This result shows that catalytic activity is falling while in use, when the conventional alumina sol is used as a binder. When not using a sol as a binder, degradation of a catalyst progresses and clarification temperature is becoming high 50%. To it, by this invention, degradation of the catalyst by thermal and mechanical stress can be eased by the effectiveness of the selected sol, and it can be equal now to the activity of long duration.

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